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(54) **Synergistic organomolybdenum compositions and lubricating compositions containing same**

Synergistische Organomolybdänumzusammensetzungen und Schmiermittelzusammensetzungen
die diese enthalten

Compositions d'organomolybdène synergistiques et compositions lubrifiantes les contenant

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(56) References cited:
WO-A-95/15368 US-A- 3 567 638
US-A- 4 648 985 US-A- 4 880 437
US-A- 4 889 647 US-A- 5 364 545

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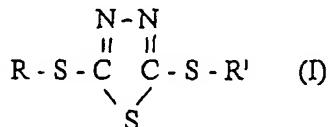
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Description**BACKGROUND OF THE INVENTION**

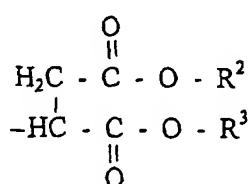
- 5 [0001] The invention concerns lubricating compositions having improved properties. Another aspect of the invention relates to additive compositions which impart antiwear and antiscuffing properties to lubricating compositions used for internal combustion engines such as gasoline engine and diesel engine.
- 10 [0002] Additives known as antiwear agents are employed to increase the load carrying capacity of lubricants. The antiwear agents promote the formation of a surface film and thereby prevent wear of the contacting surfaces. The mechanical efficiency enhanced by decreased friction loss further results in decreased fuel consumption and energy savings.
- 15 [0003] It is known that certain organic molybdenum complexes possess antiwear properties as well as other desirable lubricating characteristics as disclosed in U.S. Pat. No. 4,889,647. Surprisingly, it has been now discovered that the molybdenum complexes described therein produce a synergistic antiwear effect in combination with certain organic sulfur compounds.
- [0004] WO 95/15368 describes a lubricating oil composition comprising a base stock oil and (a) oxymolybdenum monoglyceride or oxymolybdenum diethyleate amide and (b) a metal dithiocarbamate. The lubricating composition is described as exhibiting improved wear resistance and copper corrosiveness and a low coefficient of friction.
- 20 [0005] US 5,364,545 describes a lubricating oil composition comprising (a) a lubricating oil basestock, (b) an organomolybdenum compound and (c) a zinc dithiophosphate salt or a zinc dithiocarbamate salt. The lubricating oil compositions are described to have a low coefficient of friction and reduced copper corrosion.

SUMMARY OF THE INVENTION

- 25 [0006] According to the invention, there are provided synergistic antiwear compositions comprising:
- (1) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex, and
- 30 (2) an organic sulfur compound selected from the group consisting of
- (i) 1,3,4-thiadiazole compounds of the formula:

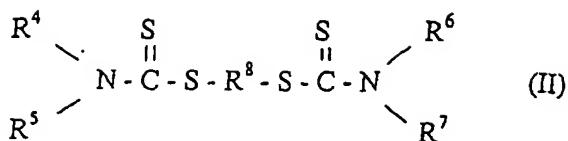


40 wherein R and R' are independently selected from C₁₋₂₂-alkyl groups, terpene residue and maleic acid residue of the formula

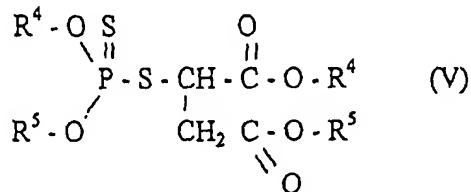


50 and R² and R³ represent C₁₋₂₂-alkyl and C₅₋₇-cycloalkyl groups, either R² or R³ may be hydrogen and either R or R' may be hydrogen when R² or R³ are C₉₋₂₂-alkyl groups;

55 (ii) bisdithiocarbamate compounds of the formula



wherein R⁴, R⁵, R⁶, and R⁷ are aliphatic hydrocarbyl groups having 1 to 13 carbon atoms and R⁸ is an alkylene group having 1 to 8 carbon atoms; and
 10 (iii) phosphorodithioate esters of the formula



20 wherein R⁴ and R⁵ may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms; and the ratio of the molybdenum complex to the sulfur compound is 1:5 to 5:1.

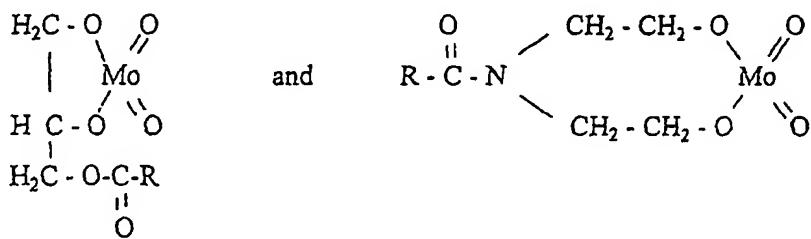
[0007] Another aspect of the invention concerns lubricating compositions having improved lubricating properties and comprising a major portion of an oil of lubricating viscosity and

25 0.1 to 10.0 percent by weight of a composition comprising (1) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (2) a sulfur compound of the formula I, II, or V.

30 DETAILED DESCRIPTION OF THE INVENTION

[0008] The organomolybdenum component of the invention is prepared by sequentially reacting fatty oil, diethanolamine and a molybdenum source by the condensation method described in U.S. Pat. No. 4,889,647. The reaction yields a reaction product mixture. The major components are believed to have the structural formulae

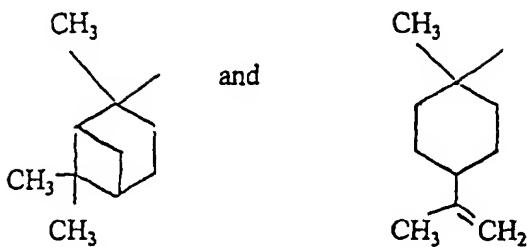
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wherein R represents a fatty oil residue. The preferred fatty oils are glycerol esters of higher fatty acids containing at least 12 carbon atoms and may contain 22 carbon atoms and higher. Such esters are commonly known as vegetable and animal oils. Vegetable oils particularly useful are oils derived from coconut, corn, cottonseed, linseed, peanut, soybean and sunflower seed. Similarly, animal fatty oils such as tallow may be used.

[0009] The source of molybdenum is an oxygen-containing molybdenum compound capable of reacting with the intermediate reaction product of fatty oil and diethanolamine to form an ester-type molybdenum complex. The source of molybdenum includes, among others, ammonium molybdates, molybdenum oxides and mixtures thereof.

[0010] The 1,3,4-thiadiazoles of formula I may be prepared by the method disclosed in U.S. Pat. No. 4,761,482 and U.S. Pat. No. 4,880,437. Terpene residues are preferably derived from pinene and limonene having the structural formulae given hereinbelow.



[0011] The alkyl groups represented by R and R¹ contain preferably 1 to 22 carbon atoms and may be branched or straight chain. Particularly preferred are compounds wherein both alkyl groups together contain a total of at least 22 carbon atoms. Groups R² and R³ in the formula I represent branched or straight chain alkyl groups containing 1 to 22 carbon atoms and cyclic aliphatic groups such as cyclohexyl, cyclopentyl and cycloheptyl.

[0012] The bisdithiocarbamates of formula II are known compounds described in U.S. Pat. No. 4,648,985. The compounds are characterized by groups R⁴ to R⁷ which are the same or different and are hydrocarbyl groups having 1 to 13 carbon atoms. The group R⁸ is an aliphatic group such as straight and branched alkylene groups containing 1 to 8 carbons. Particularly preferred is methylenebis (dibutylthiocarbamate) available commercially under the tradename

20 VANLUBE® 7723 from R.T. Vanderbilt Company, Inc.

[0013] The phosphorodithioate esters of the formula V are known compounds. One of the processes of manufacture is disclosed in U.S. Pat. No. 3,567,638 Groups R⁴ and R⁵ in the formula V may be the same or different and may be selected from branched and straight chain alkyl groups. Preferred are groups containing 1 to 8 carbon atoms.

[0014] The sulfur compounds are known to possess certain lubricating properties such as oxidation, wear and corrosion inhibition in various lubricating media. Sometimes, however, the sulfur compounds alone do not provide adequate antiwear protection for the varied heavy duty applications of many industrial and automotive lubricants.

[0015] Moreover, under certain conditions, the high concentrations of sulfur compounds may produce an adverse effect on the overall performance of the lubricant.

[0016] Unexpectedly, the above sulfur compounds produce synergistic antiwear effect when combined with organomolybdenum compounds in certain ratios. Synergism is displayed by compositions containing 1 to 5 parts by weight of the sulfur compound to 5 to 1 part by weight of the molybdenum compound.

[0017] Another advantage of the synergistic combination is that the compositions possess good antioxidant properties. Even in instances where the sulfur compounds do not possess an antioxidant activity, the combination with the molybdenum complexes provides a composition with good overall antioxidant properties.

[0018] The synergistic compositions may be incorporated in any lubricating media by known methods. The compositions impart antiwear as well as oxidation inhibiting and extreme pressure properties to natural and synthetic lubricants formulated as oils or greases.

[0019] The base oils employed as lubricant vehicles are typical natural and synthetic oils used in automotive and industrial applications such as, among others, turbine oils, hydraulic oils, gear oils, crankcase oils and diesel oils.

[0020] Natural base oils include mineral oils, petroleum oil, paraffinic oils and the ecologically desirable vegetable oils. Typical synthetic oils include pentaerythritol esters, poly-alpha-olefins, hydrogenated mineral oils, silicones and silanes.

[0021] The compositions of the invention may be incorporated in the lubricant in an amount effective to produce the desired antiwear characteristics. An amount from 0.1 to 10.0 percent will be sufficient for most applications. A preferred range is from 0.5 to 3.0 percent by weight of the total lubricant composition.

[0022] The lubricating compositions may contain other conventional additives depending on the intended use of the lubricant. For example, formulations may contain rust inhibitors such as metal salts of alkyl naphthalenesulfonic acids, demulsifiers, dispersants, detergents and supplemental antioxidants, particularly alkylated diphenylamines.

[0023] The grease formulations may contain various thickening agents such as, among others, silicate minerals, metal soaps and organic polymers.

[0024] The following examples are given for the purpose of illustrating the invention and are not intended in any way to limit the invention. All percentages and parts are based on weight unless otherwise indicated.

EXAMPLE 1

[0025] [0024] A laboratory test was conducted by using the original Falex machine to simulate the valve train wear of an automobile engine. The V-blocks and pin were washed in mineral spirits with an ultrasonic cleaner, rinsed with acetone, air dried and weighed. The test sample (60 g) was placed into the oil cup. The motor was switched on and the loading arm was placed on the ratchet wheel. Upon reaching the reference load of 227 kg, the ratchet wheel was disengaged

and the load was maintained constant for 3.5 hours. Thereafter, the motor was switched off. The V-blocks and pin were washed, dried and weighed. The weight loss, a measure of wear, was recorded and compiled in Table I.

[0025] The test was performed with a molybdenum complex in conjunction with the following ashless sulfur compound synergists of the invention: S-dicarbobutoxyethyl 0,0-dipropylphosphorodithioate (hereinafter phosphorodithioate ester) and methylenebis-(dibutylthiocarbamate). The molybdenum complex was a reaction product of coconut oil, 2,2'-iminobisethanol and hexammonium salt of molybdic acid. The base oil was a hydrofinished naphthenic oil (ISO VG 22 manufactured by Sun Refining and Marketing Co.).

[0026] The results compiled in Table I indicate that the molybdenum complex and the above sulfur compounds act as synergists towards inhibition of wear.

Table I

Modified Falex Wear Test Component, Mass Percent						
Sample	1	2	3	4	5	6
Molybdenum complex	1.0	1.5	--	0.5	--	0.5
Phosphorodithioate ester	--	--	1.0	0.5	--	--
Methylenebis(dibutylthiocarbamate)	--	--	--	--	1.5	1.0
Test Parameters						
Test Time, min.	40*	75*	20*	210	210	210
Total Weight Loss, mg.	433	542.8	--	14.6	86.4	3.4

*Test terminated due to excessive wear

EXAMPLE 2 (not according to the invention)

[0027] The modified Falex Wear Test described in Example 1 was performed with the same molybdenum complex in conjunction with the following metal salts of the sulfur compound synergists: nickel dilauryldithiocarbamate, calcium di-2-ethylhexylthiophosphate, aluminum di-2-ethylhexylthiophosphate, tellurium di-2-ethylhexylthiophosphate, and C₁₂₋₁₄-alkylamine salt of tert-octyl phosphates (hereinafter dithiophosphate amine salt). The base oil was a hydrofinished naphthenic oil (ISO VG 22).

[0028] The results compiled in Table II herein indicate that the molybdenum complex and the above salts of the sulfur compounds act as synergists towards inhibition of wear.

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Table II

Sample	Modified Falex Wear Test Component, Mass Percent									
	7	8	9	10	11	12	13	14	15	16
Molybdenum complex	1.5	--	0.5	--	0.5	--	0.5	--	0.5	--
Nickel dithiocarbamate	--	1.5	1.0	--	--	--	--	--	--	0.5
Calcium dithiophosphate	--	--	--	1.5	1.0	--	--	--	--	--
Aluminum dithiophosphate	--	--	--	--	--	1.5	1.0	--	--	--
Tellurium dithiophosphate	--	--	--	--	--	--	--	1.5	1.0	--
Dithiophosphate amine salts	--	--	--	--	--	--	--	--	1.5	1.0
Test Parameters										
Test Time, min.	75*	5*	210	5*	210	210	210*	210	2*	210
Total Weight Loss, mg.	542.8	366.8	14.9	366.6	90.1	33.5	18.4	84.8	17.7	5.6**
										41.9

* Test terminated due to excessive wear

**High galling fail

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EXAMPLE 3

[0029] A thin film oxygen uptake test was conducted essentially according to the method described by Chia-Soon Ju et al, J. Am. Soc. Lubricating Eng., 40, 2, 75-83, 1984. The oxidation induction time of the lubricant was measured under conditions which simulate the high temperature oxidation processes in automotive engines by modified rotary bomb oxidation test method ASTM D-2272. The test was conducted with 1.5 gram samples of hydrofinished naphthenic oil, ISO VG 22. The composition of the invention described in Example 1 and, for comparison, the individual components, were added to the oil in the amount indicated in Table III. The test was conducted at 160°C and initial oxygen pressure of 620.6 kPa (90 psi). A "pass" oil has a high induction time, while a "fail" oil has a low induction time. The compositions of the invention display good antioxidative effect as demonstrated by the data compiled in Table III.

Table III

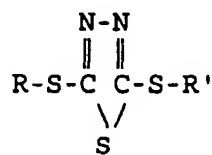
Thin Film Oxygen Uptake Test Component, Mass Percent				
Sample	18	19	20	21
Molybdenum complex	1.0	1.5	--	0.5
Methylenebis (dibutylthiocarbamate)	--		1.5	1.0
Test Parameter				
Average Induction Time, min.	10	10	75	93

[0030] The above embodiments have shown various aspects of the present invention. Other variations will be evident to those skilled in the art and such modifications are intended to be within the scope of the invention as defined by the appended claims.

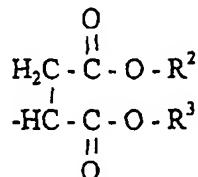
Claims

1. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (b) an organic sulfur compound selected from the group consisting of 1,3,4-thiadiazole compounds of the formula



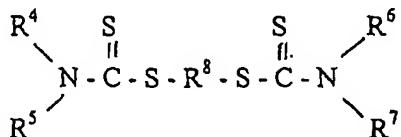
wherein R and R' are independently selected from alkyl groups having 1 to 22 carbon atoms, terpene residue and maleic acid residue of the formula:



and R² and R³ represent C₁₋₂₂-alkyl and C₅₋₇-cyloalkyl groups, and either R² or R³ may be hydrogen, and either

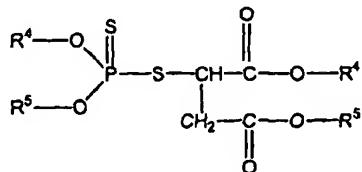
R or R¹ may be hydrogen when R² and R³ are C₉₋₂₂-alkyl groups and the ratio of the molybdenum complex to the sulfur compound is 1:5 to 5:1.

- 5 2. A composition according to claim 1 wherein the 1,3,4-thiadiazole compound is 2,5-bis(2-pinanylthio)-1,3,4-thiadiazole.
- 10 3. A synergistic antiwear composition consisting of
 (a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (b) a bisdithiocarbamate compound of the formula



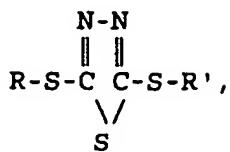
20 wherein R⁴, R⁵, R⁶ and R⁷ are aliphatic hydrocarbon groups having 1 to 13 carbon atoms and R⁸ is an alkylene group having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the bisdithiocarbamate is 1:5 to 5:1.

- 25 4. A composition according to claim 3 wherein the bisdithiocarbamate compound is methylenebis(dibutylthiocarbamate).
5. A synergistic antiwear composition consisting of
 (a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex and
 (b) a phosphorodithioate ester of the formula:

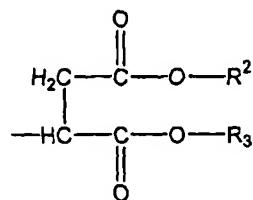


wherein R⁴ and R⁵ may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the ester is 1:5 to 5:1.

- 45 6. A composition according to claim 5 wherein the ester is S-dicarbobutoxyethyl 0,0-dipropylphosphorodithioate.
7. A lubricating composition comprising an oil of lubricating viscosity and 0.1 to 10.0 percent by weight of a synergistic antiwear composition consisting of
 (a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield 0.1 to 12.0 percent of molybdenum based on the weight of the complex and
 (b) an organic sulfur compound selected from the group consisting of:
 (i) 1,3,4-thiadiazole compounds of the formula

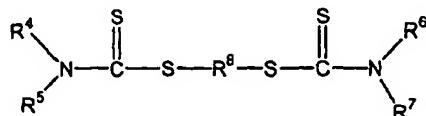


10 wherein R and R' are independently selected from alkyl groups having 1 to 22 carbon atoms, terpene residue and maleic acid residue of the formula



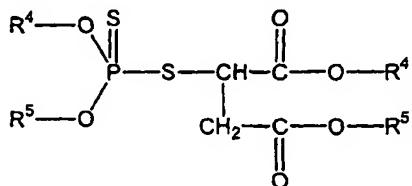
and R² and R³ represent C₁₋₂₂-alkyl and C₅₋₇-cycloalkyl groups, either R² or R³ may be hydrogen and either R or R' may be hydrogen when R² and R³ are C₉₋₂₂-alkyl groups;

25 (ii) bisdithiocarbamate compounds of the formula:



35 wherein R⁴, R⁵, R⁶ and R⁷ are aliphatic hydrocarbon groups having 1 to 13 carbon atoms and R⁸ is an alkylene group having 1 to 8 carbon atoms;

(iii) phosphorodithioate esters of the formula:



wherein R⁴ and R⁵ may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the sulfur compound is 1:5 to 5:1.

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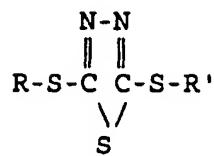
Patentansprüche

1. Synergistische Verschleißschutzzusammensetzung, die aus

- 55 a) einem molybdänorganischen Komplex, der durch Umsetzung von etwa 1 mol Fettöl, 1,0 bis 2,5 mol Diethanolamin und einer Molybdänquelle hergestellt ist, die ausreicht, 0,1 bis 12,0 % Molybdän, bezogen auf das Gewicht des Komplexes, zu ergeben, und
 b) einer organischen Schwefelverbindung besteht, die aus der Gruppe ausgewählt ist, die aus 1,3,4-Thiadia-

zolverbindungen mit der Formel

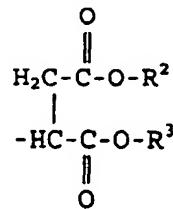
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besteht, worin R und R' unabhängig voneinander aus Alkylgruppen mit 1 bis 22 Kohlenstoffatomen, dem Terpenrest und dem Maleinsäurerest mit der Formel

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ausgewählt sind, R² und R³ C₁- bis C₂₂-Alkyl- und C₅- bis C₇-Cycloalkylgruppen bedeuten und entweder R² oder R³ und, wenn R² und R³ C₉- bis C₂₂-Alkylgruppen bedeuten, entweder R oder R' Wasserstoff bedeuten können,

wobei das Verhältnis von Molybdänkomplex zu Schwefel 1 : 5 bis 5 : 1 beträgt.

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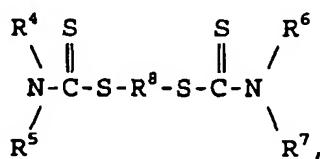
2. Zusammensetzung nach Anspruch 1, worin die 1,3,4-Thiadiazolverbindung 2,5-Bis(2-pinanylthio)-1,3,4-thiadiazol ist.
3. Synergistische Verschleißschutzzusammensetzung, die aus

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a) einem molybdänorganischen Komplex, der durch Umsetzung von etwa 1 mol Fettöl, 1,0 bis 2,5 mol Diethanolamin und einer Molybdänquelle hergestellt ist, die ausreicht, 0,1 bis 12,0 % Molybdän, bezogen auf das Gewicht des Komplexes, zu ergeben, und

b) einer Bisdithiocarbamatverbindung mit der Formel

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worin R⁴, R⁵, R⁶ und R⁷ aliphatische Kohlenwasserstoffgruppen mit 1 bis 13 Kohlenstoffatomen bedeuten und R⁸ eine Alkylengruppe mit 1 bis 8 Kohlenstoffatomen bedeutet, besteht,

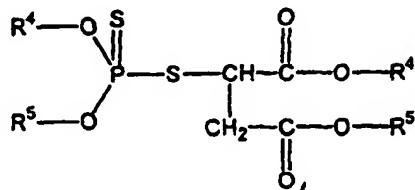
wobei das Verhältnis von Molybdänkomplex zu Bisdithiocarbamat 1 : 5 bis 5 : 1 beträgt.

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4. Zusammensetzung nach Anspruch 3, worin die Bisdithiocarbamatverbindung Methylenbis(dibutylthiocarbamat) ist.
5. Synergistische Verschleißschutzzusammensetzung, die aus

a) einem molybdänorganischen Komplex, der durch Umsetzung von etwa 1 mol Fettöl, 1,0 bis 2,5 mol Diethanolamin und einer Molybdänquelle hergestellt ist, die ausreicht, 0,1 bis 12,0 % Molybdän, bezogen auf das Gewicht des Komplexes, zu ergeben, und

b) einem Phosphorodithioatester mit der Formel



worin R^4 und R^5 gegebenenfalls voneinander verschieden sein können und aus Alkylgruppen mit 1 bis 8 Kohlenstoffatomen ausgewählt sind,

20 wobei das Verhältnis von Molybdänkomplex zu Schwefel 1 : 5 bis 5 : 1 beträgt.

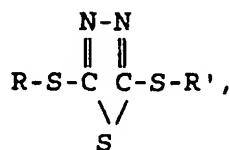
6. Zusammensetzung nach Anspruch 5, worin der Ester S-Dicarbobutoxyethyl-0,0-dipropylphosphorodithioat ist.

7. Schmiermittelzusammensetzung, die ein Öl mit Schmierviskosität und 0,1 bis 10,0 Gew.% einer synergistischen Verschleißschutzzusammensetzung umfaßt, die aus

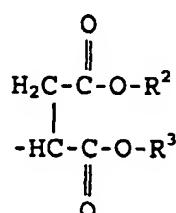
30 a) einem molybdänorganischen Komplex, der durch Umsetzung von etwa 1 mol Fettöl, 1,0 bis 2,5 mol Diethanolamin und einer Molybdänquelle hergestellt ist, die ausreicht, 0,1 bis 12,0 % Molybdän, bezogen auf das Gewicht des Komplexes, zu ergeben, und

35 b) einer organischen Schwefelverbindung besteht, die aus der Gruppe ausgewählt ist, die aus

I) 1,3,4-Thiadiazolverbindungen mit der Formel

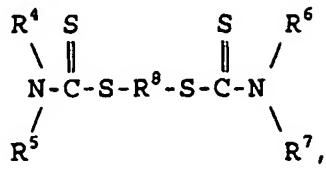


40 worin R und R' unabhängig voneinander aus Alkylgruppen mit 1 bis 22 Kohlenstoffatomen, dem Terpenrest und dem Maleinsäurerest mit der Formel



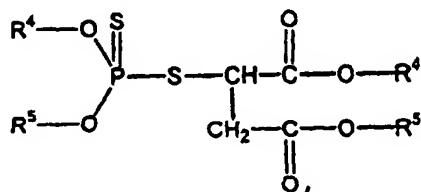
55 ausgewählt sind, R² und R³ C₁- bis C₂₂-Alkyl und C₅- bis C₇-Cycloalkylgruppen bedeuten und entweder R² oder R³ und, wenn R² und R³ C₉- bis C₂₂-Alkylgruppen bedeuten, entweder R oder R¹ Wasserstoff bedeuten können,

II) Bisdithiocarbamatverbindungen mit der Formel



worin R^4 , R^5 , R^6 und R^7 aliphatische Kohlenwasserstoffgruppen mit 1 bis 13 Kohlenstoffatomen bedeuten und R^8 eine Alkylengruppe mit 1 bis 8 Kohlenstoffatomen bedeutet, und

III) Phosphorodithioatestern mit der Formel



worin R^4 und R^5 gegebenenfalls voneinander verschieden sein können und aus Alkylgruppen mit 1 bis 8 Kohlenstoffatomen ausgewählt sind, besteht,

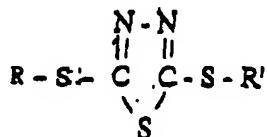
30 wobei das Verhältnis von Molybdänkomplex zu Schwefelverbindung 1 : 5 bis 5 : 1 beträgt.

Revendications

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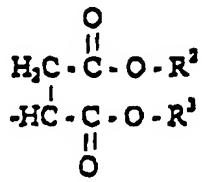
1. Composition synergique anti-usure constituée de

- (a) un complexe organomolybdène préparé en faisant réagir environ 1 mole d'huile grasse, de 1,0 à 2,5 moles de diéthanolamine et une source de molybdène suffisante pour donner de 0,1 à 12,0 pourcent de molybdène basé sur le poids du complexe et
 40 (b) un composé organique sulfuré choisi dans le groupe constitué de composés 1,3,4-thiadiazole de formule



50 où R et R', indépendamment l'un de l'autre, sont choisis parmi les groupes alkyle ayant de 1 à 22 atomes de carbone, un reste terpéique et un reste acide maléique de formule :

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et R² et R³ représentent des groupes alkyle en C₁-C₂₂ et cycloalkyle en C₅-C₇, et soit R², soit R³ peut représenter l'hydrogène, et soit R, soit R¹ peut représenter l'hydrogène lorsque R² et R³ représentent des groupes alkyle en C₉-C₂₂ et le rapport du complexe molybdène au composé sulfuré est situé dans la plage allant de 1:5 à 5:1.

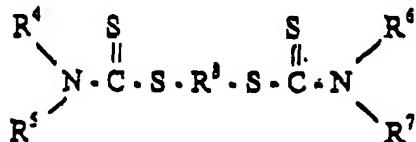
- 15 2. Composition selon la revendication 1, dans laquelle le composé 1,3,4-thiadiazole représente le 2,5-bis(2-pinanyl-thio)-1,3,4-thiadiazole.

- ### 3. Composition synergique anti-usure constituée de

20 (a) un complexe organomolybdène préparé en faisant réagir environ 1 mole d'huile grasse, de 1,0 à 2,5 moles de diéthanolamine et une source de molybdène suffisante pour donner de 0,1 à 12,0 pourcent de molybdène basé sur le poids du complexe et

(b) un composé bisdithiocarbamate de formule

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35 où R⁴, R⁵, R⁶ et R⁷ représentent des groupes hydrocarbonés aliphatiques ayant de 1 à 13 atomes de carbone et R⁸ est un groupe alkylène ayant de 1 à 8 atomes de carbone, et le rapport du complexe molybdène au bisdithiocarbamate est situé dans la plage allant de 1:5 à 5:1.

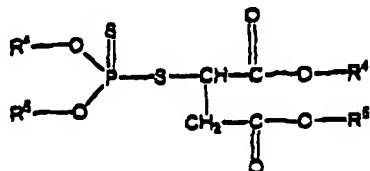
4. Composition selon la revendication 3, dans laquelle le composé bisdithiocarbamate représente le bis(dibutylthiocarbamate) de méthylène.

- #### 40 5. Composition synergique anti-usure constituée de

(a) un complexe organomolybdène préparé en faisant réagir environ 1 mole d'huile grasse, de 1,0 à 2,5 moles de diéthanolamine et une source de molybdène suffisante pour donner de 0,1 à 12,0 pourcent de molybdène basé sur le poids du complexe et

(b) un ester de type phosphorodithioate de formule :

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où R⁴ et R⁵ peuvent être les mêmes ou différente et sont choisis parmi les groupes alkyle ayant de 1 à 8 atomes de carbone, et le rapport du complexe molybdène à l'ester est situé dans la plage allant de 1:5 à 5:1.

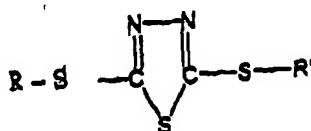
6. Composition selon la revendication 5, dans laquelle l'ester représente le S-dicarbobutoxyéthyl 0,0-dipropylphosphorodithioate.

5 7. Composition lubrifiante comprenant une huile de viscosité lubrifiante et de 0,1 à 10,0 pourcent en poids d'une composition synergique anti-usure constituée de

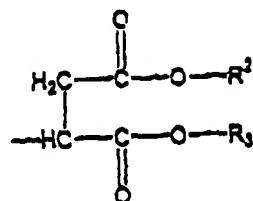
10 (a) un complexe organomolybdène préparé en faisant réagir environ 1 mole d'huile grasse, de 1,0 à 2,5 moles de diéthanolamine et une source de molybdène suffisante pour donner de 0,1 à 12,0 pourcent de molybdène basé sur le poids du complexe et

(b) un composé organique sulfuré choisi dans le groupe constitué de :

(i) composés 1,3,4-thiadiazole de formule

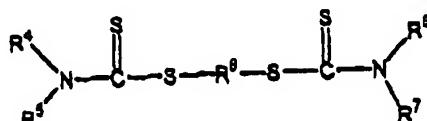


20 où R et R¹, indépendamment l'un de l'autre, sont choisis parmi les groupes alkyle ayant de 1 à 22 atomes de carbone, un reste terpénique et un reste acide maléique de formule



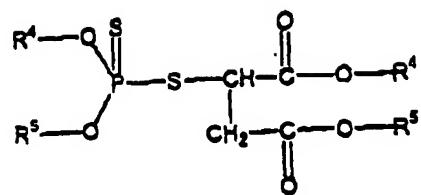
30 35 et R² et R³ représentent des groupes alkyle en C₁-C₂₂ et cycloalkyle en C₅-C₇, et soit R², soit R³ peut représenter l'hydrogène, et soit R, soit R¹ peut représenter l'hydrogène lorsque R² et R³ représentent des groupes alkyle en C₉-C₂₂ ;

(ii) composés bisdithiocarbamate de formule



45 où R⁴, R⁵, R⁶ et R⁷ représentent des groupes hydrocarbonés aliphatiques ayant de 1 à 13 atomes de carbone et R⁸ est un groupe alkylène ayant de 1 à 8 atomes de carbone ;

50 (iii) esters de type phosphorodithioate de formule :



10 où R⁴ et R⁵ peuvent être les mêmes ou différents et sont choisis parmi les groupes alkyle ayant de 1 à 8 atomes de carbone, et le rapport du complexe molybdène à l'ester est situé dans la plage allant de 1:5 à 5:1.

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